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(54) **Safety glass interlayer**

(57) An interlayer for safety glass including a polyvinyl chloride polymeric material has a glass transition temperature long within the range of 18°C to 21°C and a brittle point of -40°C or below, a laminate formed by sandwiching the interlayer between two sheets of glass having a log₁₀ creep compliance transition of no greater than 4.25 at a reference temperature of 150°C. The interlayer is formed of a polyvinyl chloride and ethylene-containing polymer and a plasticizer composition comprising a mixture of dihexyl adipate and dioctyl sebacate and a polycaprolactone, the interlayer then being sandwiched between two sheets of glass and being bonded to the glass by means of a silane incorporated in the polymer. The composition may optionally include heat stabilisers, antioxidants and ultraviolet radiation stabilisers. At least one of the sheets of glass may be tinted and include at least one ultraviolet radiation absorber.

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POLYVINYL CHLORIDE SAFETY GLASS INTERLAYER

The present invention relates to an interlayer for safety glass and, more particularly, to a polyvinyl chloride - containing polymeric material used as the basis for such interlayer.

Safety glass is a well known term for a glass sandwich composed of an interlayer bonding together two glass plates or sheets so that breaking the glass results in minimum dispersion of broken glass fragments. The interlayer must possess a number of properties, including the following: high impact energy adsorption to minimize concussive energy; shear and tear strength sufficient to prevent rupture of the interlayer by the broken glass; sufficient adhesion to the glass to inhibit laceration on contact with, and prevent dispersion of, broken glass; acceptable thermal heat stability and weatherability; and good optical qualities. The interlayer must possess these properties over the wide range of temperatures in which these laminated glazings are used.

It has been widely known to use a film of plasticized polyvinyl butyral as the interlayer material in safety glass for automobiles, air planes and building materials because of its high adhesiveness, transparency and good mechanical properties over a broad range of temperatures. However, the use of plasticized polyvinyl butyral films makes the production of laminated safety glass relatively expensive.

The surface of plasticized polyvinyl butyral film is very tacky, and presents a problem of blocking at the time of windup after film formation. Thus, plasticized polyvinyl butyral film must be provided with some parting means if it is to be stored or transported in the form of stacks of die-cut blanks or in the form of rolls. Furthermore, the production of

plasticized polyvinyl butyral films requires specialised equipment and, due to their sensitivity to moisture, plasticized polyvinyl butyral films must generally be handled under controlled atmosphere conditions during manufacture, storage and immediately prior to their incorporation into the laminated safety glass. This all adds to the expense of utilizing polyvinyl butyral films in laminated safety glass.

Alternative interlayer materials have been proposed. For instance, United States Patent No. 4277538 to Beckmann et al discloses a laminated safety glass employing a sheet of plasticized polyvinyl chloride (PVC) as the interlayer. The use of PVC would be advantageous in that it may be produced on conventional equipment and would be much less expensive to manufacture and process into a laminated safety glass when compared with polyvinyl butyral.

However, there are several criteria which need to be satisfied if PVC is to be used as an interlayer in safety glass, particularly in the transport field. For example the interlayer must have a low haze and a low yellowing index. The PVC must act as a carrier for the adhesive which is to be used to bond the interlayer to the glass. Moreover, the interlayer must have a glass transition temperature which is ideally in the region of 20°C. Finally, if the interlayer is to be used in articles such as vehicle windscreens, it must be readily processable.

Unfortunately, PVC on its own satisfies few, if any, of these criteria. It is extremely brittle and therefore needs to be plasticized. It is also thermally unstable and a heat stabiliser needs to be admixed therewith. Even with the addition of a plasticizer and a heat stabiliser, the impact resistance of the material remains too low to enable it to be used in,

for example, a vehicle windscreen. This latter problem could be overcome by making the PVC film thicker. Unfortunately, the additional thickness means that the film is too heavy to be used in windscreens. Additionally, thickening the film has a disadvantageous effect on the optical properties of the film in that the amount of haze is increased as is the yellowing index.

If PVC on its own is unsuitable, it appears, at first sight, to be a logical step to look at co-polymers of PVC. Such action does, indeed, have certain beneficial effects. For example, the processing temperature, which is, effectively, the autoclaving temperature if vehicle windscreens are being considered, is reduced by using a PVC co-polymer. Moreover, the use of a co-polymer tends to increase the impact strength of the film, particularly if certain chemical groupings are present. Additionally, the so-called "brittle point" of the film is improved by using a PVC co-polymer. The brittle point is defined as being the temperature at which 50% of samples fail the ASTM D-746 impact test. As will be appreciated by those skilled in the art, a better "brittle point" means that the temperature at which the samples fail the above test is lower.

Unfortunately, co-polymers of PVC also have disadvantages over PVC per se. Many co-polymers melt at a lower temperature than PVC on its own. This often means the heat stability of the co-polymer is worse. Haze is also a problem if co-polymers are used. Haze will inevitably result if there is the slightest incompatibility between the components of the co-polymer. In addition, the mixing of the components is of vital importance. If such mixing is not effected extremely accurately, it will be almost impossible to achieve a film having a low haze.

A co-polymer, on its own, will not, however, give an interlayer made therefrom the appropriate impact strength. Accordingly, plasticizers must be used and the choice of such plasticizers is of major importance. First, the plasticizer must be fully compatible with the copolymer and many conventional plasticizers are not. The plasticizer chosen must also be capable of being intimately mixed with the PVC and, if present, the heat stabilizer if low haze is to be achieved

If the plasticizer is transported to the surface of the co-polymer, a "bloom" will appear on the surface of the film and this is clearly undesirable. This is particularly true if an adhesive is present, as will usually be the case. If there is a bloom on the film, adhesion in the bloomed areas will not occur.

There are a number of conventional plasticizers which can be used with PVC copolymers. However, they all exhibit one or more of the following disadvantages :-

- (a) the impact strength of the film produced is not sufficiently high to permit the use of such an interlayer in a vehicle windscreen particularly at low temperatures;
- (b) a high temperature is required for processing the film or, alternatively, the thermal stability of the material is so poor that it cannot be processed;
- (c) The creep compliance of the mixture is such that it is not possible to produce a laminated structure having acceptable optical properties;
- (d) it is not possible to mix the two polymers and the plasticizer sufficiently well in order to ensure low haze; and
- (e) the rate of yellowing of the film in use is unacceptably fast.

When using a plasticizer or a mixture of plasticizers, a major problem arises in that if the brittle point of the interlayer is increased by so doing, the glass transition temperature is also increased. Similarly, if the use of a plasticizer causes a lowering of the brittle point, it also lowers the glass transition temperature. For automotive applications, a glass transition temperature of the order of 18°C to 20°C is necessary. The desired brittle point for such applications is of the order of -45°C or lower. At this point, it should be remarked that the relevant figures for PVC on its own are approximately 95°C and approximately 60°C respectively. Moreover, even though it might be possible to select a plasticizer or mixture of plasticizers which provide the appropriate values, it has been found that such plasticizers adversely affect the optical properties of the interlayer to such an extent that the interlayer is totally unsuitable for use in vehicle windscreens.

Accordingly, the present invention seeks to provide a plasticized PVC co-polymer which has a glass transition temperature and a brittle point which are acceptable when the polymer is used as the basis of the interlayer in a windscreen made from safety glass but which also can be processed to form a laminated structure at a temperature which is of the order of 150°C.

According to the present invention, there is therefore provided an interlayer formed of a co-polymer of PVC with ethylene, a plasticizer composition comprising a mixture of dihexyl adipate and dioctyl sebacate and a polycaprolactone, the interlayer having a glass transition temperature lying within the range of 18°C to 21°C and a brittle point of -40°C or below, such that a laminate formed from the interlayer sandwiched between two sheets of glass has a creep compliance transition having a \log_{10} value of not more than 4.25 at a

reference temperature of 150°C, the interlayer being bonded to the glass by means of a silane incorporated in the polymer.

The term "creep compliance transition" is used to give an indication of the transition of the material from a state of rubbery elasticity to a state of viscous flow. However, the term "creep compliance" is also used herein but in a manner which is slightly different to its normally understood meaning. The creep of a material is determined by plotting \log_{10} compliance against \log_{10} time (in seconds). The compliance is the reciprocal of the modulus of elasticity. When such a plot is produced, the curve generally has a substantially horizontal portion and a substantially vertical portion. The transition between these two parts of the curve is where the material begins to flow. The laminate is produced in an autoclave and the autoclave has, generally, a fifteen minute cycle. It is therefore necessary for the creep or flow to occur before the end of such fifteen minutes. If the time can be reduced substantially below fifteen minutes, this means that the autoclaving temperature can be reduced. Our aim, therefore, is to cause the creep or flow to take place as near to fifteen minutes as possible so as to give the minimum autoclave temperature. The term "creep compliance transition" as used herein denotes the temperature at which this is achieved. It is preferred if the \log_{10} value is no greater than 4.25 at a reference temperature of 150°C.

Preferably, the PVC- containing polymer comprises a PVC resin having a degree of polymerisation of less than 1000 in admixture with an ethylene containing resin. Advantageously, the ethylene-containing resin is a copolymer containing 84 mol% vinyl chloride and 16 mol% ethylene.

Further preferably, the PVC resin is present in an amount of from 55 to 65 phr.

Desirably, the ethylene-containing resin is present in an amount of from 25 to 35 phr.

Further advantageously, the polycaprolactone is present in an amount of from 7 to 12 phr, optimally 8phr.

Further desirably, the dihexyl adipate is present in an amount of from 10 to 15 phr, optimally 12phr. Similarly, the dioctyl sebacate is desirably present in an amount of from 15 to 30 phr, optimally 28 phr.

Still further advantageously, the silane is a secondary aminosilane. In such a case, it is desirable if the silane is an aromatic secondary aminosilane, particularly N-(3-trimethoxysilyl) propyl benzenamine.

Other materials may be present in the interlayer composition. Thus, for example, one or more of the following classes of materials may be present:-

- (a) heat stabilisers;
- (b) antioxidants;
- (c) ultraviolet radiation stabilisers;

The preferred heat stabilisers are organometallic salts such as salts of alkaline earth or selected transition metals. Such metals include aluminium, barium, cadmium, calcium, lead, magnesium, tin and zinc. The particularly preferred heat stabilisers are a mixture of zinc and barium salts or a mixture of calcium and barium salts. If included in the composition, these heat stabilisers are preferably present in an amount of 2 to 4 phr, optimally 3 phr. Secondary heat stabilisers such as epoxidised soya bean oil may also be present in the composition in an amount of up to 5 phr.

The antioxidant, if included, is present in an amount of up to 1 phr, optimally 0.5 phr. Similarly, the ultraviolet radiation absorber, if included, is present in an amount of up to 0.5 phr, optimally 0.2 phr. The silane incorporated in the polymer to cause adhesion of the glass to the polymer to form the laminate is present in an amount of up to 1 phr, optimally 0.75 phr.

It is surprising that the above-described system provides an interlayer of suitable quality to be laminated with glass to form windscreens for automotive vehicles. We believe that it is the combination of features which provide the desired results and that these results could not be anticipated by those skilled in the art. By way of explanation, we would point out that copolymers on their own will not provide the necessary impact strength. They must be plasticised and the necessary plasticisers must be capable of being intimately mixed with the copolymer, conventional plasticisers such as dioctyl adipate and dioctyl phthalate were initially tried. Unfortunately, the creep compliance, in other words, the processing temperature needed to produce the laminate, was too high to produce laminates having acceptable optical properties or the impact resistance was too low to be acceptable. Attempts were made to overcome these problems by increasing the amount of plasticiser employed to very high levels of the order of 50 to 60 phr. This still proved unsuccessful.

A different plasticizer, namely dihexyl adipate, was then tried. The use of such compound did, indeed, improve the low temperature impact resistance but, at the same time, the glass transition temperature fell to approximately 3°C. In other words, whilst improving the impact resistance at low temperatures, the impact resistance at ambient

temperature, say 18°C was considerably reduced. It therefore appeared impossible to provide an interlayer having the desired properties.

A mixture of plasticizers was then tried. In particular, a mixture of dihexyl adipate and benzyl butyl phthalate was employed. Whilst this improved certain characteristics of the interlayer, it adversely affected the creep compliance, that is to say, the processing temperature, the optical quality of the interlayer and also required the film to be made excessively thick to obtain the other desired properties.

An attempt was then made to modify the PVC-containing polymer. However, this also proved unsuccessful in that certain properties could be improved but only at the expense of other properties. To give an example of the surprising aspect of the present invention, we utilised a specific PVC resin having a degree of polymerisation of 1300 and found that this was no better than any of the other resins we had tried. However, we surprisingly found that the same resin differing only in that it had a degree of polymerisation of 950 could provide the necessary properties but only if the resin contained other specific additives.

In particular, we found that the mixing of the PVC resin with the vinyl chloride-ethylene comonomer had to be carefully controlled. Such resin and comonomer system needs to be plasticised but any plasticizer added is preferentially taken up by the comonomers. The PVC resin is starved of plasticizer and will not, therefore, mix well with the comonomer.

Moreover, we found it necessary to add a caprolactone to the resin-comonomer system. Caprolactones are known to be plasticizers for PVC and also to be processing

aids in that they will lower the temperature at which autoclaving of a laminate can be effected. However, the amount of caprolactone used hitherto was generally in the region of 1-2% by weight (corresponding, very approximately to 1-2 phr). It is well known that relatively large amounts of caprolactone accelerate the rate of haze formation and that as the amount of caprolactone is increased, the glass transition temperature is decreased. Whilst we wish to attain a glass transition temperature of 18 to 20°C, we do not wish it to drop too low. To prevent this happening, the quantity of the other plasticizers in the system must be reduced but, by so doing, the creep compliance and the brittle point of the laminated structure is adversely affected. Contrary to all expectations, we have found that if the caprolactone is present in an amount of about 10 phr, not only do we achieve the desired plasticity and processing temperature but also the laminate has good optical properties, brittle point and glass transition temperature.

The invention will be further described, by way of illustration only, with reference to the following non-limitative Examples.

EXAMPLE 1

An interlayer, approximately 0.8mm (30 to 33mils) thick was made using the following formulation :-

<u>Component</u>	<u>phr</u>
SE950 PVC Resin ¹	60
VE-U ²	30
CAPA 650 ³	10
Dihexyl adipate	12.8

Diocetyl sebacate	19.2
UBZ 7910 ⁴	3
Drapex 6.8 ⁵	5
Irganox 1010 ⁶	0.5
CPL 46 ⁷	0.1
Tinuvin 328 ⁸	0.2
Y-9669 ⁹	1.0

In the above list, "phr" denotes parts per hundred of resin.

1. PVC resin having a degree of polymerization of 950 available from Shintech Inc. of Freeport, Texas.
2. A copolymer resin (84% vinyl chloride - 16% ethylene monomer mixture) available from Sekisui Fine Chemical Co. Ltd. of Osaka, Japan.
3. Polycaprolactone resin available from Solvay Interlox
4. A barium/zinc stabilizer package available from Baerlocher G.m.b.H. of Munich, Germany.
5. Epoxidised soybean oil available from Witco Corp. of Oakland, New Jersey.
6. A hindered phenolic antioxidant available from Ciba-Geigy Corp. of Hawthorn, New York.
7. A perchlorate stabilizer available from Asahi Denka Kogyo K.K. of Japan.
8. Benzotriazole ultraviolet light stabilizer available from Ciba-Geigy Corp.
9. N-(3-methoxysilyl) propyl benzenamine available from Union Carbide Corporation.

The above interlayer was produced by mixing the components in, initially, a high speed mixer and then in an intensive shear-type mixer. The mixers are both heated so that the temperature of the interlayer rises to approximately 160°C. The interlayer is then subjected to the action of two sequential two-roll mills and is thereafter calendered. Laminates are then produced by applying glass sheets to opposed sides of the interlayer and are autoclaved at approximately 150°C and at 240 psi with a 45 minute hold time.

Clear laminates were obtained which had the following properties :-

Adhesion, initial (pummel)	9
Haze, initial	0.8%
Heat Stability (yellowing index)	1.19

The laminates had a brittle point of -41°C and a glass transition temperature of 18.0°C.

The laminates also had a creep compliance transition of 3.95.

EXAMPLE 2

Example 1 was repeated with the exceptions that a) Baerlocher JD 60-2 was used instead of UBZ 7910, b) no Irganox 1010 was used and c) the amount of Tinuvin 328 was increased to 0.75 phr. Baerlocher JD 60-2 is a calcium/zinc stabilizer package also available from Baerlocher G.m.b.H.. Again, clear laminates were produced having the following properties :-

Adhesion, initial (pummel)	9
Haze, initial	0.5
Yellowing index	0.95

The brittle point, glass transition temperature and the creep compliance transition of the laminates were identical to those of Example 1, that is to say, -41°C , 18.0°C and 3.95.

The interlayer may be sandwiched between two layers of glass, at least one of which is tinted and has good ultraviolet absorption properties. The colorant in the tinted glass may be selected from the group consisting of iron, cerium and titanium oxides or mixtures thereof. The ultraviolet transmittance of the tinted glass at 2.1 mm is preferably below 68%, ideally below 56%, in the range of 300 nm to 400 nm.

CLAIMS

1. An interlayer formed of a co-polymer of polyvinyl chloride with ethylene, a plasticizer composition comprising a mixture of dihexyl adipate and dioctyl sebacate and a polycaprolactone, the interlayer having a glass transition temperature lying within the range 18°C to 21°C, a brittle point of -40°C or below and a creep compliance transition no greater than 4.25 (log₁₀) seconds at a reference temperature of 150°C.
2. An interlayer as claimed in claim 1 in which the polyvinyl chloride containing polymer comprises a polyvinyl chloride resin having a degree of polymerisation of less than 1000 in admixture with an ethylene containing resin.
3. An interlayer as claimed in claim 1 or 2 in which the ethylene containing resin is a copolymer containing 84 mol% vinyl chloride and 16 mol% ethylene.
4. An interlayer as claimed in any one of claims 1 to 3 in which the polyvinyl chloride resin is present in an amount of from 55 phr to 65 phr.
5. An interlayer as claimed in any preceding claim in which the ethylene containing resin is present in an amount of from 25 phr to 35 phr.

6. An interlayer as claimed in any preceding claim in which the polycaprolactone is present in an amount of from 7 phr to 12 phr.
7. An interlayer as claimed in claim 6 in which the polycaprolactone is present in an amount of 8 phr.
8. An interlayer as claimed in any preceding claim in which the dihexyl adipate is present in an amount of from 10 phr to 15 phr.
9. An interlayer as claimed in claim 8 in which the dihexyl adipate is present in an amount of 12 phr.
10. An interlayer as claimed in any preceding claim wherein the dioctyl sebacate is present in an amount of from 15 phr to 30 phr.
11. An interlayer as claimed in claim 10 in which the dioctyl sebacate is present in an amount of 28 phr.
12. An interlayer as claimed in any preceding claim wherein the silane is N-(3-trimethoxysilyl) propyl benzenamine.

13. An interlayer as claimed in claim 12 wherein the N-(3-trimethoxysilyl) propyl benzenamine is present in an amount of 1 phr.
14. An interlayer as claimed in any preceding claim additionally containing at least one material selected from the group consisting of heat stabilisers, antioxidants and ultraviolet radiation stabilisers.
15. An interlayer as claimed in claim 13 in which the heat stabiliser is an organometallic salt.
16. An interlayer as claimed in claim 15 in which the organometallic salt is a salt of a metal selected from the group consisting of aluminium, barium, cadmium, calcium, lead, magnesium, tin and zinc and mixtures thereof.
17. An interlayer as claimed in claim 16 in which the heat stabiliser is a mixture of zinc and barium salts.
18. An interlayer as claimed in claim 16 in which the heat stabiliser is a mixture of zinc and calcium salts.
19. An interlayer as claimed in any one of claims 15 to 18 in which the heat stabiliser is present in an amount of from 2 phr to 4 phr.

20. An interlayer as claimed in claim 19 in which the heat stabiliser is present in an amount of 3 phr.
21. An interlayer as claimed in any one of claims 15 to 21 additionally including a secondary heat stabiliser in the form of epoxidised soybean oil.
22. An interlayer as claimed in claim 21 in which the epoxidised soybean oil is present in an amount of up to 5 phr.
23. An interlayer as claimed in any one of claims 14 to 22 in which the antioxidant is present in an amount of up to 1 phr.
24. An interlayer as claimed in claim 23 in which the antioxidant is present in an amount of 0.5 phr.
25. An interlayer as claimed in any one of claims 14 to 24 in which the ultraviolet radiation absorber is present in an amount of up to 0.5 phr.
26. An interlayer as claimed in claim 25 in which the ultraviolet absorber is present in an amount of 0.2 phr.

27. An interlayer as claimed in any preceding claim sandwiched between two sheets of glass, at least one of the sheets being a tinted glass including one or more colorants, at least one of the colorants being an absorber of ultraviolet radiation.
28. An interlayer as claimed in claim 27 in which the ultraviolet absorber in the tinted glass is selected from the group consisting of oxides of iron, cerium and titanium and mixtures thereof.
29. An interlayer as claimed in claim 27 or 28 in which the tinted glass has an ultraviolet transmission of less than 68% over the range of 300 nm to 400 nm at a thickness of 2.1 mm.
30. An interlayer as claimed in claim 29 in which the absorber has an ultraviolet transmission of less than 56% over the range of 300 nm to 400 nm at a thickness of 2.1 mm.
31. An interlayer as claimed in claim 1 substantially as hereinbefore described with reference to the foregoing Examples.



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Claims searched: 1-31

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3M(MXC)

Int Cl (Ed.6): B32B

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	None	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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